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UTILITY PATENT APPLICATION TRANSMITTAL

(Only for new nonprovisional applications under 37 CFR 1.53(b))

Attorney Docket No.	00-012	*Total Pages*	42
First Named Inventor or Application Identifier	DENNIS P. CURRAN ET AL.		
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APPLICATION ELEMENTS

See MPEP chapter 600 concerning utility patent application contents.

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Attorney's Docket No. 00-012 **PATENT**

Applicant or Patentee: Dennis P. Curran et al.

Application or Patent No.: / to be assigned

Filed or Issued: June 22, 2000

For: **FLUOROUS TIN COMPOUNDS AND METHODS OF USING FLUOROUS TIN COMPOUNDS**

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FLUOROUS TIN COMPOUNDS AND METHODS OF USING FLUOROUS TIN COMPOUNDS,

by inventor(s) Dennis P. Curran, Zhiyong Luo and Sabine Hadida

described in

[x] the specification filed herewith.

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TITLE

FLUOROUS TIN COMPOUNDS AND METHODS OF USING FLUOROUS TIN COMPOUNDS

Governmental Interests

This invention was made with government support under grant GM33372 awarded by the National Institutes of Health. The government has certain rights in this invention.

Field of the Invention

The present invention relates to fluorous tin compounds and to methods of using fluorous tin compounds, and, especially, to fluorous tin reaction components that are easily separated from non-fluorous compounds via fluorous separation techniques.

Background of the Invention

Organic compounds are typically synthesized by reactions in which a starting material or reactant is contacted with one or more other reactants, reagents, or catalysts to form a new organic product. The separation of the desired products from any added reactants, reagents or catalysts (and/or from any byproducts derived from such reaction components) can be tedious and time consuming.

Accordingly, improved methods for the separation of organic reaction products from other reaction components are needed.

Along these lines, the use of fluorous reagents, reactants and catalysts has recently begun to offer attractive new options. The use of such fluorous techniques is illustrated in general terms in Figure 1. An organic (non-fluorous) starting material or reactant is contacted with a fluorous reactant, reagent or catalyst, possibly with other non-fluorous reaction components, and typically in a solvent, to form a new organic product or mixture of products. The organic product(s) are then separated from the unreacted fluorous reactant, reagent or catalyst and any other fluorous byproducts derived therefrom by simple fluorous-organic phase separation techniques such as liquid-liquid separation and/or solid-liquid separation. Such techniques have been described, for example, in US Patent Nos. 5,777,121 and 5,859,247, the disclosures of which are incorporated herein by reference.

Organotin reactants, reagents and catalysts are a powerful class of molecules that effect many useful transformations of organic starting materials or reactants to organic products. Accordingly, the use of organotin compounds is common practice in organic synthesis. See, for example, Davies, A. G. *Organotin Chemistry*; VCH: Weinheim, pp 327 (1997) and *Chemistry of Tin*; 2nd ed.; Smith, P. J., Ed.; Blackie: London, pp 578 (1997). However, the separation of the newly formed, non-tin containing organic products from the remaining tin compounds in the reaction mixture is notoriously difficult and improvements in separation techniques are needed to unlock the potential power of organic reactions mediated by organotin compounds.

Many of the most popular types of organotin reagents have the formula R_3SnX, where R is an alkyl group, often butyl, and X is a group which is involved in the reaction with an organic substrate. A few among many possible examples of such compounds include Bu_3SnH, Bu_3SnN_3, Bu_3SnCl and Bu_3SnPh. Recently, fluorous analogs of these compounds have been introduced. The fluorous analogs are generally designed to accomplish reactions similar to the corresponding non-fluorous compound but to facilitate separation after reaction. In currently available fluorous tin reagents, each of the three alkyl groups R is replaced by a spacer group Rs attached to a fluorous group Rf according to the following general formula: $[(Rf)Rs)]_3SnX$. Examples of such fluorous tin reagents include $(C_6F_{13}CH_2CH_2)_3SnH$, $(C_6F_{13}CH_2CH_2)_3SnN_3$, $(C_6F_{13}CH_2CH_2)_3SnCl$, $(C_6F_{13}CH_2CH_2)_3SnPh$, etc.

Illustrative examples of the uses of one of these fluorous tin reagents, $(C_6F_{13}CH_2CH_2)_3SnH$, are shown in Figure 2. Reduction of adamantyl bromide with 1 equiv of $(C_6F_{13}CH_2CH_2)_3SnH$ followed by fluorous-organic liquid-liquid extraction provides the organic product adamantane on evaporation of the organic liquid phase and the fluorous product $(C_6F_{13}CH_2CH_2)_3SnBr$ on evaporation of the fluorous phase. A similar reduction can be conducted in a more economical way by using a catalytic amount of the fluorous tin hydride along with an inexpensive inorganic reductant like sodium cyanoborohydride. A three-phase liquid extraction then provides the respective products: inorganic salts (from the aqueous phase), adamantane (from the organic phase), and the tin hydride catalyst (from the fluorous phase).

While currently available fluorous tin reagents provide advantages over the traditional (non-fluorous)

trialkyltin class of reagents, some disadvantages remain that restrict the broad application thereof. For example, existing reagents with three fluorous chains can have low solubility in organic solvents. This low solubility can lead to problems in selecting suitable reaction solvents since it is often desirable that the tin compounds have substantial solubility under the reaction conditions. For example, the reactions in Figure 2 require a non-standard solvent or co-solvent such as benzotrifluoride. Moreover, the large numbers of fluorines in currently available fluorous tin reagents result in compounds of high molecular weight, which is a detraction from the standpoint of expense and atom economy. Finally, certain classes of organotin reagents, for example Bu_2SnO, have fewer than three alkyl chains and cannot be rendered fluorous by current strategies.

It is thus very desirable to develop fluorous reaction compounds or components that substantially reduce or eliminate such problems.

Summary of the Invention

The present invention provides fluorous tin reaction components (that is, reagents, reactants and/or catalysts) bearing only two or one fluorous groups or chains. Surprisingly, even though the fluorous reaction components of the present invention have many fewer fluorines than currently available fluorous reagents, the fluorous reaction components of the present invention can still be separated efficiently from organic (non-fluorous) reaction components by fluorous separation techniques. In addition, the fluorous tin reaction components of the present invention can be substantially more soluble in

organic reaction solvents. Thus, the scope of application in chemical reactions of the fluorous tin reaction components of the present invention is dramatically increased without compromising the scope of separation. These features, coupled with lower molecular weight and increased atom economy, give the fluorous tin reaction components of the present invention significant advantages over currently available fluorous reagents.

In one aspect, the present invention provides a method of carrying out a reaction comprising the steps of:

mixing at least one organic reaction component with at least one fluorous reaction component having the formula:

$$X^1Sn(R)_n[Rs(Rf)]_{3-n},\ X^1X^2Sn[Rs(Rf)]_2 \text{ or } O{=}Sn[Rs(Rf)]_2$$

wherein n is 1 or 2, R is a C_1-C_6 alkyl group, X^1 and X^2 are independently, the same or different, H, F, Cl, Br, I, N_3, OR^1, OOR^1 SR^1, SeR^1, CN, NC, NR^1R^2, an aryl group, a heteroaryl group, an alkyl group of 1 to 20 carbons, an alkenyl group, an alkynyl group, $-C(O)R^3$ (an acyl group), $M((Rs')(Rf'))_3$, $OM((Rs')(Rf'))_3$ or $OOM((Rs')Rf'))_3$, wherein M is Si, Ge, or Sn, and wherein R^1 and R^2 are each independently the same or different H, an alkyl group, $-SO_2R^3$ or $-C(O)R^3$, wherein R^3 is an alkyl group or an aryl group, and wherein Rs and Rs' are each independently the same or different a spacer group, and wherein Rf and Rf' are each independently the same or different a fluorous group;

carrying out a reaction to produce an organic product; and

after producing the organic product, separating any excess of the fluorous reaction component and any fluorous byproduct of the fluorous reaction component using a fluorous separation technique.

As used herein, the term "fluorous", when used in connection with an organic (carbon-containing) molecule, moiety or group, refers generally to an organic molecule, moiety or group having a domain or a portion thereof rich in carbon-fluorine bonds (for example, fluorocarbons or perfluorocarbons, fluorohydrocarbons, fluorinated ethers and fluorinated amines). Fluorous compounds generally preferentially partition into a fluorous phase during fluorous-organic phase separation. For example, perfluorinated ether groups can have the general formula $-[(CF_2)_xO(CF_2)_y]_zCF_3$, wherein x, y and z are integers. Perfluorinated amine groups can, for example, have the general formula $-[(CF_2)_x(NR^a)CF_2)_y]_zCF_3$, wherein R^a can, for example, be $-(CF_2)_nCF_3$, wherein n is an integer. Fluorous ether groups and fluorous amine groups suitable for use in the present invention need not be perfluorinated, however. As used herein, the term "perfluorocarbons" refers generally to organic compounds in which all hydrogen atoms bonded to carbon atoms have been replaced by fluorine atoms. The terms "fluorohydrocarbons" and "hydrofluorocarbons" include organic compounds in which at least one hydrogen atom bonded to a carbon atom has been replaced by a fluorine atom. A few examples of suitable fluorous groups Rf and Rf' for use in the present invention include, but are not limited to, $-C_4F_9$, $-C_6F_{13}$, $-C_8F_{17}$, $-C_{10},F_{21}$, $-C(CF_3)_2C_3F_7$, $-C_4F_8CF(CF_3)_2$, $-CF_2CF_2OCF_2CF_2OCF_3$ and $-CF_2CF_2(NCF_3)CF_2CF_2CF_3$.

Perfluoroalkyl groups and hydrofluoroalkyl groups are well suited for use in the present invention. For example, Rf and Rf′ can independently be a linear perfluoroalkyl group of 3 to 20 carbons, a branched perfluoroalkyl group of 3 to 20 carbons, and a hydrofluoroalkyl group of 3 to 20 carbons. Hydrofluoroalkyl groups preferably include up to one hydrogen atom for each two fluorine atoms. In the case of perfluoralkyl groups and hydrofluoroalkyl groups, Rf and Rf′ are preferably a linear perfluoroalkyl group of 6 to 12 carbons, a branched perfluoroalkyl group of 6 to 12 carbons, or a hydrofluoroalkyl group of 6 to 12 carbons.

In another aspect, the present invention provides a chemical compound of the formula

$$X^1Sn(R)_n[Rs(Rf)]_{3-n},$$

wherein n is 1 or 2, R is a C_1-C_6 alkyl group, X^1 is H, F, Cl, Br, I, N_3, OR^1, OOR^1 SR^1, SeR^1, CN, NC, NR^1R^2, an aryl group, a heteroaryl group, an alkyl group of 1 to 20 carbons, an alkenyl group, an alkynyl group, $-C(O)R^3$, $M((Rs')(Rf'))_3$, $OM((Rs')(Rf'))_3$ or $OOM((Rs')Rf'))_3$, wherein M is Si, Ge, or Sn, and wherein R^1 and R^2 are each independently the same or different H, an alkyl group, $-SO_2R^3$ or $-C(O)R^3$, wherein R^3 is an alkyl group or an aryl group, and wherein Rs and Rs′ are each independently the same or different an alkylene group of 1 to 6 carbons or a phenylene group, and wherein Rf and Rf′ are each independently a fluorohydrocarbon group, a perfluorocarbon group, a fluorinated ether group or a fluorinated amine group.

In another aspect, the present invention provides chemical compound having the formula:

$$O=Sn[Rs(Rf)]_2$$

wherein Rs is an alkylene group of 1 to 6 carbons or a phenylene group and wherein Rf is a fluorohydrocarbon group, a perfluorocarbon group, a fluorinated ether group or a fluorinated amine group. Such molecules can exist as oligomers or polymers with the formula $(O=Sn[Rs(Rf)]_2)_n$.

In still a further aspect, the present invention provides a chemical compound having the formula:

$$X^1X^2Sn[Rs(Rf)]_2$$

wherein X^1 and X^2 are independently, the same or different, H, N_3, OR^1, OOR^1 SR^1, SeR^1, CN, NC, NR^1R^2, a heteroaryl group, an alkyl group of 2 to 20 carbons, an alkenyl group, an alkynyl group, $-COR^3$, $M((Rs')(Rf'))_3$, $OM((Rs')(Rf'))_3$ or $OOM((Rs')Rf'))_3$, wherein M is Si, Ge, or Sn, and wherein R^1 and R^2 are each independently the same or different H, an alkyl group, $-SO_2R^3$ or $-COR^3$, wherein R^3 is an alkyl group or an aryl group, wherein Rs and Rs' are each independently the same or different an alkylene group of 1 to 6 carbons or a phenylene group, and wherein Rf and Rf' are each independently a fluorohydrocarbon group, a perfluorocarbon group, a fluorinated ether group or a fluorinated amine group.

In several embodiments, X^1 and/or X^2 are (independently), for example, an allyl group, Br, F, Cl, I or H. In several other embodiments, Rs is an alkylene group (preferably, $-CH_2CH_2-$), and/or Rf is a perfluoroalkyl group.

Separation of the fluorous reaction components of the present invention and any fluorous byproducts thereof from organic products and other organic compounds is achieved by using fluorous separation techniques that are based upon differences between/among the fluorous nature of a mixture of compounds. As used herein, the term "fluorous separation technique" refers generally to a method that is used to separate mixtures containing fluorous molecules or organic molecules bearing fluorous domains from each other and/or from non-fluorous compounds based predominantly on differences in the fluorous nature of molecules (for example, size and/or structure of a fluorous molecule or domain or the absence thereof). Fluorous separation techniques include but are not limited to solid phase extraction or chromatography over solid fluorous phases such as fluorocarbon bonded phases or fluorinated polymers. See, for example, Danielson, N.D. et al., "Fluoropolymers and Fluorocarbon Bonded Phases as Column Packings for Liquid Chromatography," J. Chromat., 544, 187-199 (1991) and Curran, D. P.; Hadida, S.; He, M. *J. Org. Chem. 62*, 6714 (1997). Examples of suitable fluorocarbon bonded phases include commercial Fluofix® and Fluophase™ columns available from Keystone Scientific, Inc. (Bellefonte, PA), and FluoroSep™-RP-Octyl from ES Industries (Berlin, NJ). Other fluorous separation techniques include liquid-liquid based separation methods such as liquid-liquid extraction or

countercurrent distribution with a fluorous solvent and an organic solvent.

The terms "alkyl", "aryl", and other groups refer generally to both unsubstituted and substituted groups unless specified to the contrary. Unless otherwise specified, alkyl groups are hydrocarbon groups and are preferably C_1-C_{15} (that is, having 1 to 15 carbon atoms) alkyl groups, and more preferably C_1-C_{10} alkyl groups, and can be branched or unbranched, acyclic or cyclic. The above definition of an alkyl group and other definitions apply also when the group is a substituent on another group. The term "aryl" refers generally to an unsubstituted or substituted phenyl (Ph) group or napthyl group.

The term "heteroaryl group" refers generally to an aromatic ring of five or six atoms in which one or more of the atoms is oxygen, nitrogen, or sulfur. The heteroaryl groups or rings can be substituted or unsubstituted and can be isolated or fused to benzo rings. Examples of isolated heteraryl rings include, but are not limited to, furan rings. Examples of benzo-fuzed heteraryl ring include, but are not limited to, benzofurans.

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The term "alkenyl" refers generally to a straight or branched chain hydrocarbon group with at least one double bond, preferably with 2-15 carbon atoms, and more preferably with 3-10 carbon atoms (for example, $-CH=CHR^c$ or $-CH_2CH=CHR^c$, wherein R^c is, for example, H or an alkyl group). The term "alkynyl" refers generally to a straight or branched chain

hydrocarbon group with at least one triple bond, preferably with 2-15 carbon atoms, and more preferably with 3-10 carbon atoms (for example, $-C{\equiv}CR^c$ or $-CH_2C{\equiv}CR^c$). The term "alkylene" refers generally to bivalent forms of an alkyl group. The term "phenylene group" refers generally to bivalent forms of an a phenyl group ($-C_6H_4-$) wherein the two groups attached thereto are situated ortho, meta or para.

The groups set forth above, can be substituted with a wide variety of substituents. For example, alkyl and alkylene groups can preferably be substituted with a group or groups including, but not limited to, halide(s), alkenyl groups, alkynyl and aryl groups. Aryl groups and heteroaryl groups can preferably be substituted with a group or groups including, but not limited to, halide(s), alkyl group(s), cyano group(s) and nitro group(s). As used herein, the terms "halide" or "halo" refer to fluoro, chloro, bromo and iodo. Preferred halide substituents are F and Cl.

Brief Description of the Drawings

Figure 1 illustrates use of fluorous reagents in organic synthesis.

Figure 2 illustrates an example of use of the fluorous tin reagent $(C_6F_{13}CH_2CH_2)SnH$ in the reduction of adamantyl bromide.

Figure 3 illustrates an example of synthesis of fluorous tin reagents of the present invention bearing one fluorous group.

Figure 4 illustrates a series of reactions with fluorous tin reagents of the present invention.

Figure 5 illustrates an example of synthesis of fluorous tin reagents of the present invention bearing two fluorous groups.

Detailed Description of the Invention

The fluorous tin reagents of the present invention can generally be made by modification of reactions known to those skilled in the art of organotin chemistry. See, for example, Davies, A. G. *Organotin Chemistry*; VCH: Weinheim, pp 327 (1997) and *Chemistry of Tin*; 2nd ed.; Smith, P. J., Ed.; Blackie: London, pp 578 (1997). For example, Grignard reagents such as $Rf(CH_2)_nMgI$, organolithium reagents $Rf(CH_2)_nLi$, or related organometallic reagents can be reacted with known tin electrophiles $Y_2Sn(X)R$ to give $(Rf(CH_2)_n)_2Sn(X)R$. In tin reagent $Y_2Sn(X)R$, Y is a leaving group. There are many types of leaving groups known to those skilled in the art and examples of some of the preferred groups Y for the current invention are chloride, bromide or triflate. In another approach, alkenes such as $Rf(CH_2)_{n-2}CH=CH_2$ can be hydrostannated with $H_2Sn(X)R$ via radical or metal catalyzed reactions to give $(Rf(CH_2)_n)_2Sn(X)R$.

The interchange of groups X in $(Rf(CH_2)_n)_2SnRX$ for other groups X is well known to those skilled in the art and can be accomplished by large classes of reactions wherein a nucleophilic precursor of the product X group (for example, cyanide, azide, alkoxide, RMgBr, etc.) replaces the leaving group X (for example a halogen or a triflate, etc.) in the

tin precursor (for example, stannylation of an alcohol), by reactions wherein a tin nucleophile (X = metal) adds to or substitutes an electrophilic precursor of the product X group (for example, allylation of a tin metal reagent with an allyl halide), by reactions wherein the Sn-X bond adds to a multiple bond (for example, hydrostannation of a carbon-carbon or carbon-oxygen double bond), or by reactions involving electrophilic cleavage of an Sn-X bond (for example, conversion of a tin hydride or vinyl or aryl tin to a tin bromide by reaction with dibromine). Other types of reactions to exchange X groups, including metal catalyzed reactions such as Stille and related couplings, are also used.

Analogous transformations are possible starting from $YSn(R)_2X$ or $HSn(R)_2X$ to make $Rf(CH_2)_nSnR_2X$ reagents. Examples that illustrative a few of the many possibilities are shown in Figure 3. Fluorous iodides **1a-c** were converted to appropriate organometallic derivatives, which were in turn reacted with allyldimethyltin to give the new tin reagents **2a-c** bearing one fluorous chain. These fluorous allyltin reagents can be used for the allylation of various organic molecules such as aldehydes under standard reaction conditions. They can also be used to make other fluorous tin reagents. For example, reaction of **2a-c** with dibromine generated tin bromides **3a-c**. These tin bromides can be reacted with a wide range of nucleophiles to make other new fluorous tin reagents. In the example of Figure 3, tin bromides were reacted with lithium aluminum hydride to make the tin hydrides **4a-c**.

Some of the advantages of the fluorous tin reagents of the present invention are illustrated by the series of reactions of Figure 4. Reduction of napthyl ethyl

iodide with tin hydrides **4b** and **4c** under the standard conditions, followed by rapid solid phase extraction over fluorous reverse phase silica gel, provided pure 2-ethyladamantane in a simple and effective reaction and separation process. This simple separation compares very favorably to the use of the standard reagent Bu_3SnH, which requires careful chromatographic separation or application of some other specialized separation technique. Moreover, the currently available fluorous reagent $(C_6F_{13}CH_2CH_2)_3SnH$ is not expected to form the product efficiently under these conditions because it is insoluble or nearly insoluble in t-butanol. A suitable solvent or cosolvent like benzotrifluoride is be needed in that case.

An example of a fluorous tin reagent bearing two fluorous chains is $(C_6F_{13}CH_2CH_2)_2SnO$, for which a synthetic route is shown in Figure 5. The synthetic route of Figure 5 modifies an approach reported synthesis of Bu_2SnO, and like the standard alkyl tin oxide, the fluorous alkyltin oxide is not monomeric but instead appears to exists as oligomers and/or polymers. See Kong, X.; Grindley, B.; Bakshi, P.K.; Cameron, T.S. *Organometallics*. 12, 4881 (1993). Reaction of the Grignard reagent derived from **1a** in suitable stoichiometry gave the bis-phenyltin reagent **5a**, which was converted to the bis-chloroacetate **6a**. Exposure of this reagent to hydroxide gave the tin oxide **7a**.

Among other uses, the mono-functionalization of diols is one of the most popular applications of Bu_2SnO. Martinelli and coworkers have recently introduced a catalytic variant of the traditional stoichiometric procedure, but the tin catalyst must still be separated from the desired organic product. See Martinelli, M. J., *et al. Org. Lett.*, 1, 447 (1999). As shown in Figure 5, the tin

oxide reaction components of the present invention can also be used to catalyze the mono-tosylation of diols under the conditions reported by Martinelli. No fluorinated reaction solvent or cosolvent is needed. Simple purification of the crude reaction mixture by liquid-liquid extraction or solid-liquid extraction provided the pure organic tosylate (organic phase) separate from the recovered tin oxide **7a** (fluorous phase). The recovered tin oxide **7a** can be reused.

Experimental

Example 1a.

Allyl-dimethyl-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)stannane (2a). Freshly prepared allyldimethyltin chloride (2.86 g, 12.7 mmol) was added dropwise to the Grignard reagent of $C_6F_{13}CH_2CH_2MgI$, which was prepared from $C_6F_{13}CH_2CH_2I$ (6.0 g, 12.7 mmol) and magnesium powder (0.37 g, 15.2 mmol). The reaction mixture was refluxed overnight (16 h) before quenching with 1N HCl. The crude product was purified by vacuum distillation (112°C/water pump) to give pure **2a** as a colorless oil (3.20 g, 35%). ^{1}H NMR ($CDCl_3$) δ 5.95 – 5.86 (m, 1H), 4.85 – 4.80 (dd, J = 16.8,1.4 Hz, 1H), 4.73 – 4.69 (dd, J = 11.8, 1.8 Hz, 1H), 2.30 – 2.12 (m, 2H), 1.83 (d, J = 8.5 Hz, 2H), 1.00 – 0.92 (m, 2H), 0.15 (s, J_{Sn-H} = 26.3 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 136.8, 121.8 – 107.2 (m), 27.9 (t), 16.9, –1.8, –12.2; ^{19}F NMR ($CDCl_3$) δ –81.3 (3F), –117.2 (2F), –122.5 (2F), –123.4 (2F), –123.9 (2F), –126.7 (2F); ^{119}Sn NMR (C_6D_6): δ –1.4; HRMS: calc. 496.9597 (M^+ – Me), found: 496.9583. IR (thin film): 1626 cm $^{-1}$.

Example 1b.

Allyl-dimethyl-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)stannane (2b). To a solution of $C_8F_{17}CH_2CH_2I$ (3.34 g, 5.82 mmol) in dry ether (50 mL) and dry hexanes (50 mL) at -78 °C was added ^tBuLi (7.5 mL, 1.7 M in pentane). After stirring at -78 °C for 30 min, freshly prepared allyldimethyl tinchloride (1.46 g, 6.47 mmol) was added slowly. The reaction mixture was stirred at −78°C for 1 h and allowed to warm to room temperature in two to three hours before quenching with water. After extraction between ether and water, the ether phase was dried over $MgSO_4$. The crude product was purified by flash chromatography with n-heptane to give **2b** as a clear oil (2.15 g, 58%). ^1H NMR ($CDCl_3$) δ 5.95 – 5.86 (m, 1H), 4.85 – 4.69 (dd, J = 17.0, 1.1 Hz, 2H), 2.30 – 2.12 (m, 2H), 1.83 (d, J = 8.7 Hz, 2H), 1.00 – 0.92 (m, 2H), 0.15 (s, J_{Sn-H} = 26.1 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 136.8, 119.2 – 108.2 (m), 28.0 (t), 17.1, −1.6; ^{19}F NMR ($CDCl_3$) δ −81.0 (3F), −116.9 (2F), −122.2 (6F), −122.3 (2F), −123.6 (2F), −126.3 (2F); ^{119}Sn NMR (C_6D_6) δ −1.39; HRMS: calcd. 622.9690 (M^+ – Me), found: 622.9685; IR (thin film): 1626 cm^{-1}.

Example 1c.

Allyl-dimethyl-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heneicosafluorododecyl)stannane (2c). This compound was prepared with the same procedure as for **2b**. Yield: 83% (clear oil). ^1H NMR ($CDCl_3$) δ 5.98 – 5.83 (m, 1H), 4.87 –

4.80 (dd, J = 16.6, 1 Hz, 1H), 4.74 – 4.70 (dd, J = 9.6, 1 Hz, 1H), 2.30 – 2.12 (m, 2H), 1.83 (d, J = 8.6 Hz, 2H), 1.00 – 0.94 (m, 2H), 0.15 (s, J_{Sn-H} = 26.1 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 136.8, 121.9 – 106.9 (m), 28.0 (t), 17.1, –1.6, –11.8; ^{19}F NMR ($CDCl_3$) δ –80.9 (3F), –116.9 (2F), –122.0 (10F), –122.9 (2F). –123.6 (2F), –126.3 (2F); ^{119}Sn NMR (C_6D_6) δ –0.47; HRMS: Calcd. 722.9626 (M^+ – Me), found: 722.9623; IR (thin film): 1626 cm^{-1}

Example 2a.

Dimethyl-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)stannane (4a). Br_2 (0.43 g, 2.68 mmol) was added to a solution of **2a** (1.20g, 2.23 mmol) in dry ether (10 mL) at 0 °C. The brown reaction mixture was further stirred at room temperature for 1.5 h. After evaporation of solvent, the residue was partitioned between CH_2Cl_2 and FC-72. The CH_2Cl_2 phase was further washed with FC-72 for three times. The crude tin bromide **3a** was dissolved in dry ether (10 mL) and cooled to -78 °C, to which LAH (2.1 mL, 1.0 M in ether) was added. The reaction was quenched with water after stirring at -78 °C for three hours. The crude mixture was further purified by column chromatography with heptane to give **4a** as a clear oil (0.72 g, 65% for two steps). ^1H NMR (C_6D_6) δ 4.75 (s, 1H), 2.03 – 1.85 (m, 2H), 0.78 – 0.60 (m, 2H), –0.7 (s, J_{Sn-H} = 17.2 Hz, 6H); ^{13}C NMR (C_6D_6) δ 122.2 – 107.5 (m), 28.5 (t), –3.0, –13.4; ^{19}F NMR ($CDCl_3$) δ –81.2 (3F), –117.1 (2F), –122.4 (2F), –123.4 (2F), –123.9 (2F), –126.6 (2F); ^{119}Sn NMR (C_6D_6)

δ −86.8; HRMS: calcd. 496.9597, found: 496.9563. IR (thin film): 1839 cm^{-1}.

Example 2b.

Dimethyl-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)stannane (4b). This compound was prepared with the same procedure as for **4a**. Overall yield for two steps: 53% (clear oil). ^{1}H NMR (C_6D_6) δ 4.74 (s, 1H), 2.03 – 1.85 (m, 2H), 0.72 – 0.66 (m, 2H), −0.07 (s, J_{Sn-H}= 28.2 Hz, 6H); ^{13}C NMR (C_6D_6) δ 120.0 – 108.4 (m), 29.3 (t), −2.4, −12.8; ^{19}F NMR ($CDCl_3$) δ −81.1 (3F), −116.3 (2F), −121.8 (6F), −122.9 (2F), −123.3 (2F), −126.3 (2F); ^{119}Sn NMR (C_6D_6) δ −86.8; HRMS: calcd. 596.9533, found: 596.9543. IR (thin film): 1841 cm^{-1}.

Example 2c.

Dimethyl-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heneicosafluorododecyl)stannane (4c). This compound was prepared with the same procedure as for **4a**. Overall yield for two steps: 85% (clear oil). ^{1}H NMR (C_6D_6) δ 4.75 (s, 1H), 2.05 – 1.87 (m, 2H), 0.73 – 0.67 (m, 2H), −0.07 (s, J_{Sn-H} = 28.1 Hz, 6H); ^{13}C NMR (C_6D_6) δ 120.3 – 108.2 (m), 29.2 (t), −2.4, −12.5; ^{19}F NMR ($CDCl_3$): δ −81.2 (3F), −114.7 (2F), −121.9 (10F), −122.4 (2F), −122.9 (2F), −126.9 (2F); ^{119}Sn NMR (C_6D_6) δ −86.9; HRMS: calcd. 696.9469 found: 696.9462. IR (thin film): 1840 cm^{-1}.

Example 3.

Measurement of the Partition Coefficient of Fluorous Tin hyrides 4a-c. Fluorous tin hydrides (2 – 12 mg) were stirred with FC-72 (1 mL) and benzene (1 mL) or acetonitrile (1 mL) for 10 min. After separation, n-octadecane was added to both phases as an internal standard (for FC-72 phase, the solvent was evaporated and ethyl acetate (1 mL) was added to dissolve both the tin hydride and n-ocadecane). An aliquot (10 uL) of each phase was injected to GC for three times and the relative peak area was used to calculate the following partition coefficients of tin hydrides: FC-72/CH3CN, **4a**, 2.4; **4b**, 14; **4c**, 48; FC-72/benzene, **4a**, 0.7; **4b**, 2.5; **4c**, 4.7.

Example 4.

General Procedure for the Reduction of 2-(2-iodoethyl)naphthalene with Fluorous Tin Hydrides. The iodide (0.5 mmol), fluorous tin hydride (0.05 mmol) and sodium cyanoborohydride (0.75 mmol) were suspended in *tert*-butanol (0.1 – 0.15 M for iodide). After flushing 5 min with argon, the reaction mixture was irradiated with a sunlamp overnight. After removal of solvent by evaporation, the residue was extracted with ether and water. The ether phase was dried and passed through a short column of fluorous reverse phase silica gel (bonded phase $-OSi(Me)_2CH_2CH_2C_6F_{13}$) eluting with acetonitrile or 85/15 methanol/water. The organic fraction was evaporated and analyzed by proton NMR spectroscopy.

Example 5.

Bis(perfluorohexylethyl)diphenyltin (5a).

In a dry round bottom flask, anhydrous ether (10 ml) was added to Mg (0.40 g, 16.37 mmol). Under nitrogen, perfluorohexylethyl iodide **1a** (0.517 g, 1.09 mmol) was added dropwise, and the flask was sonicated for 30 min. The rest of the perfluorohexylethyl iodide (4.65 g, 9.89 mmol) was added slowly over 5 min, and the mixture was refluxed for 2 h, during which the mixture turned dark green. After 2 h, a solution of diphenyltin dichloride (1.50 g, 4.36 mmol) in benzene (15 ml) was added via a cannula. The resulting mixture was refluxed for 4 h with stirring. The mixture was cooled and quenched with 1M HCl (2x5 ml) and sat. NH_4Cl (2x30 ml). The organic layer was dried over $MgSO_4$. Removal of solvent yielded a mixture of 3.68 g of a brown amorphous solid. ^1H NMR analysis showed it to be 7/1 mixture of bis(perfluorohexylethyl)diphenyltin **5a** and dimer $(C_6F_{13}CH_2CH_2)_2$: ^1H NMR (300MHz, $CDCl_3$) δ 1.41-1.47 (t, 4H), 2.07-2.18 (t,4H), 2.25-2.40 (m, 4H), 7.38-7.44 (m, 10H). ^{19}F NMR (282MHz,$CDCl_3$ with $CFCl_3$): δ -126.69, -123.85, -123.42, -122.49, -117.00, -114.91, -81.32.

Example 6.

Bis(perfluorohexylethyl)tin bis(chloroacetate) (6a).

In a round bottom flask, the mixture of **5a** and dimer (2.28 g, 2.36 mmol) and chloroacetic acid (0.45 g, 4.72 mmol) were combined. The mixture was heated to 160°C for 20 min. A white precipitate formed on cooling. Hexanes

(25 ml) were added, and the mixture was refluxed until the precipitate dissolved. After cooling, the residue was filtered, and yielded 1.68 g (73%) bis(perfluorohexylethyl)tin bis(chloroacetate) **6a**: ^{1}H NMR (300MHz, $CDCl_3$): δ1.67-1.93 (t, 4H), 2.46-2.57 (m, 4H), 4.16 (s, 4H); ^{19}F NMR (282MHz, $CDCl_3$): δ -126.69, -123.78, -123.43, -122.46, -116.55, -81.30.

Example 7.

Bis(perfluorohexylethyl)tin Oxide (7a).

In a round bottom flask **6a** (0.1 g, 0.11 mmol) was taken up in ether (5 ml). 2.5M NaOH (0.132 ml, 0.33 mmol) was added, and the mixture was stirred for 1 h. Hexanes (20 ml) was added and the resulting mixture was transferred to a separatory funnel. The mixture was washed with sat. 1N HCl (2x5 ml) and NH_4Cl (2x20 ml). The organic layer was dried over $MgSO_4$. Removal of solvent yielded 0.34 g (76%) bis(perfluorohexylethyl)tin oxide **7a**: ^{1}H NMR (300MHz, acetone-d_6): δ2.50-2.61 (broad band, 4H), 2.77-2.84 (t, 4H); ^{19}F NMR (282 MHz, acetone-d_6 with $CFCl_3$): δ -125.69, -122.84, -122.35, -121.37, -115.17, -80.56; ^{119}Sn NMR (111.8 MHz, $CDCl_3$ with $(CH_3)_4Sn$): δ -167.23.

Example 8.

General Procedure for Catalyzed Tosylation of 1-phenyl-1,2-ethane diol.

In a round bottom flask, 1-phenyl-1,2-ethane diol (1 mmol) was dissolved in CH_2Cl_2 (5 ml). Triethylamine (1 mmol) and tin oxide **7a** (0.02 mmol) were added. Tosyl chloride was added and the solution was stirred for 50 min. After addition of H_2O (1 ml), the mixture was transferred to a separatory funnel. The aqueous layer was washed with dicholormethane (2x10ml). The combined organic layers were was with H_2O (2x25ml) and brine (2x25ml). The organic layer was dried over $MgSO_4$. Removal of solvent yielded a mixture of toluene-4-sulfonic acid-2-hydroxy-2-phenyl ethyl ester and tin oxide **7a**. The mixture can be separated by either liquid-liquid or solid-liquid extraction.

Procedure for liquid-liquid extraction with FC-72.

A mixture of toluene-4-sulfonic acid-2-hydroxy-2-phenyl ethyl ester and tin oxide **7a** was taken up in dichloromethane (25ml) and transferred to a separatory funnel.. The resulting mixture was washed with FC-72 (8x25ml). The dichloromethane was evaporated to yield toluene-4-sulfonic acid-2-hydroxy-2-phenyl ethyl ester and the FC-72 was evaporated to yield **7a**.

Prodedure for solid phase extraction with fluorous silica gel.

A mixture of toluene-4-sulfonic acid-2-hydroxy-2-phenyl ethyl ester and tin oxide **7a** was taken up in a mixture of 9/1 methanol : water. The resulting mixture was transferred to a column containing fluorous reverse phase silica gel (bonded phase $-OSi(Me)_2CH_2CH_2C_6F_{13}$) (100mg). The column was then washed with a mixture of 9/1 methanol : water (3ml), followed by THF (3ml). Evaporation of the methanol : water mixture yielded toluene-4-sulfonic acid-2-hydroxy-2-phenyl ethyl ester.

Although the present invention has been described in detail in connection with the above examples, it is to be understood that such detail is solely for that purpose and that variations can be made by those skilled in the art without departing from the spirit of the invention except as it may be limited by the following claims.

WHAT IS CLAIMED IS:

1. A method of carrying out a reaction comprising the steps of:

mixing at least one organic reaction component with a fluorous reaction component having the formula:

$$X^1Sn(R)_n[Rs(Rf)]_{3-n},\ X^1X^2Sn[Rs(Rf)]_2 \text{ or } O{=}Sn[Rs(Rf)]_2$$

wherein n is 1 or 2, R is a C_1-C_6 alkyl group, X^1 and X^2 are independently, the same or different, H, F, Cl, Br, I, N_3, OR^1, OOR^1, SR^1, SeR^1, CN, NC, NR^1R^2, an aryl group, a heteroaryl group, an alkyl group of 1 to 20 carbons, an alkenyl group, an alkynyl group, $-C(O)R^3$, $M((Rs')(Rf'))_3$, $OM((Rs')(Rf'))_3$ or $OOM((Rs')Rf'))_3$, wherein M is Si, Ge, or Sn, and wherein R^1 and R^2 are each independently the same or different H, an alkyl group, $-SO_2R^3$ or $-C(O)R^3$, wherein R^3 is an alkyl group or an aryl group, and wherein Rs and Rs' are each independently the same or different a spacer group, and wherein Rf and Rf' are each independently the same or different a fluorous group;

carrying out a reaction to produce an organic product; and

after producing the organic product, separating any excess of the fluorous reaction component and any fluorous byproduct of the fluorous reaction component using a fluorous separation technique.

2. The method of Claim 1 wherein X^1 and X^2 are independently the same or different an allyl group, Br, Cl, F, I, or H, Rs is $-CH_2CH_2-$, and Rf is a perfluoroalkyl group.

3. The method of Claim 1 wherein Rf is a fluorohydrocarbon group, a perfluorocarbon group, a fluorinated ether group or a fluorinated amine group.

4. The method of Claim 1 wherein Rf is a linear perfluoroalkyl group of 3 to 20 carbons, a branched perfluoroalkyl group of 3 to 20 carbons, and a hydrofluoroalkyl group of 3 to 20 carbons, the hydrofluoroalkyl group comprising up to one hydrogen atom for each two fluorine atoms.

5. The method of Claim 1 wherein Rf is a linear perfluoroalkyl group of 6 to 12 carbons, a branched perfluoroalkyl group of 6 to 12 carbons, or a hydrofluoroalkyl group of 6 to 12 carbons, the hydrofluoroalkyl group comprising up to one hydrogen atom for each two fluorine atoms.

6. The method of Claim 1 wherein R^3 is a perfluoroalkyl group.

7. The method of Claim 1 wherein Rs is an alkylene group or a phenylene group.

8. The method of Claim 1 wherein Rs is an alkylene group.

9. A method for carrying out a chemical reaction, comprising the steps of:

combining at least one fluorous reaction component having the formula:

$$X^1Sn(R)_n[Rs(Rf)]_{3-n},\ X^1X^2Sn[Rs(Rf)]_2 \text{ or } O{=}Sn[Rs(Rf)]_2$$

wherein n is 1 or 2, R is a C_1-C_6 alkyl group, X^1 and X^2 are independently, the same or different, H, F, Cl, Br, I, N_3, OR^1, OOR^1 SR^1, SeR^1, CN, NC, NR^1R^2, an aryl group, a heteroaryl group, an alkyl group of 1 to 20 carbons, an alkenyl group, an alkynyl group, $-C(O)R^3$, $M((Rs')(Rf'))_3$, $OM((Rs')(Rf'))_3$ or $OOM((Rs')Rf'))_3$, wherein M is Si, Ge, or Sn, and wherein R^1 and R^2 are each independently the same or different H, an alkyl group, $-SO_2R^3$ or $-C(O)R^3$, wherein R^3 is an alkyl group or an aryl group, and wherein Rs and Rs' are each independently the same or different a spacer group, and wherein Rf and Rf' are each independently the same or different a fluorous group, and at least one organic reaction component convertible in the presence of the fluorous reaction component to a product in an organic solvent;

contacting the fluorous reaction component and the organic reaction component in the organic solvent under conditions suitable to produce the product; and

after production of the product, separating any excess of the fluorous reaction component and any fluorous byproduct of the fluorous reaction component using a fluorous separation technique.

10. A chemical compound having the formula:

$$X^1Sn(R)_n[Rs(Rf)]_{3-n},$$

wherein n is 1 or 2, R is a C_1-C_6 alkyl group, X^1 is H, F, Cl, Br, I, N_3, OR^1, OOR^1 SR^1, SeR^1, CN, NC, NR^1R^2, an aryl group, a heteroaryl group, an alkyl group of 1 to 20 carbons, an alkenyl group, an alkynyl group, $-C(O)R^3$, M((Rs')(Rf'))$_3$, OM((Rs')(Rf'))$_3$ or OOM((Rs')Rf'))$_3$, wherein M is Si, Ge, or Sn, and wherein R^1 and R^2 are each independently the same or different H, an alkyl group, $-SO_2R^3$ or $-C(O)R^3$, wherein R^3 is an alkyl group or an aryl group, and wherein Rs and Rs' are each independently the same or different an alkylene group of 1 to 6 carbons or a phenylene group, and wherein Rf and Rf' are each independently a fluorohydrocarbon group, a perfluorocarbon group, a fluorinated ether group or a fluorinated amine group.

11. The compound of Claim 10 wherein X^1 is an allyl group, Br, Cl, F, I, or H, Rs is $-CH_2CH_2-$, and Rf is a perfluoroalkyl group.

12. The compound of Claim 10 wherein Rf is a fluorohydrocarbon group, a perfluorocarbon group, a fluorinated ether group or a fluorinated amine group.

13. The compound of Claim 10 wherein Rf is a linear perfluoroalkyl group of 3 to 20 carbons, a branched perfluoroalkyl group of 3 to 20 carbons, and a hydrofluoroalkyl group of 3 to 20 carbons, the

hydrofluoroalkyl group comprising up to one hydrogen atom for each two fluorine atoms.

14. The compound of Claim 10 wherein Rf is a linear perfluoroalkyl group of 6 to 12 carbons, a branched perfluoroalkyl group of 6 to 12 carbons, or a hydrofluoroalkyl group of 6 to 12 carbons, the hydrofluoroalkyl group comprising up to one hydrogen atom for each two fluorine atoms.

15. The compound of Claim 10 wherein R^3 is a perfluoroalkyl group.

16. The compound of Claim 10 wherein Rs is an alkylene group of 1 to 6 carbons.

17. A chemical compound having the formula:

$$O=Sn[Rs(Rf)]_2$$

wherein Rs is an alkylene group of 1 to 6 carbons or a phenylene group and wherein Rf is a fluorohydrocarbon group, a perfluorocarbon group, a fluorinated ether group or a fluorinated amine group.

18. The compound of Claim 17 wherein Rs is an alkylene group of 1 to 6 carbons.

19. A chemical compound having the formula:

$X^1X^2Sn[Rs(Rf)]_2$

wherein X^1 and X^2 are independently, the same or different, H, N_3, OR^1, OOR^1 SR^1, SeR^1, CN, NC, NR^1R^2, a heteroaryl group, an alkyl group of 2 to 20 carbons, an alkenyl group, an alkynyl group, $-C(O)R^3$, $M((Rs')(Rf'))_3$, $OM((Rs')(Rf'))_3$ or $OOM((Rs')Rf'))_3$, wherein M is Si, Ge, or Sn, and wherein R^1 and R^2 are each independently the same or different H, an alkyl group, $-SO_2R^3$ or $-C(O)R^3$, wherein R^3 is an alkyl group or an aryl group, wherein Rs and Rs' are each independently the same or different an alkylene group of 1 to 6 carbons or a phenylene group, and wherein Rf and Rf' are each independently a fluorohydrocarbon group, a perfluorocarbon group, a fluorinated ether group or a fluorinated amine group.

20. The compound of Claim 19 wherein Rs is an alkylene group of 1 to 6 carbons.

ABSTRACT

A method of carrying out a reaction comprising the steps of: mixing at least one organic reaction component with at least one fluorous reaction component having the formula:

$$X^1Sn(R)_n[Rs(Rf)]_{3-n},\ X^1X^2Sn[Rs(Rf)]_2 \text{ or } O{=}Sn[Rs(Rf)]_2$$

wherein n is 1 or 2, R is a C_1-C_6 alkyl group, X^1 and X^2 are independently, the same or different, H, F, Cl, Br, I, N_3, OR^1, OOR^1 SR^1, SeR^1, CN, NC, NR^1R^2, an aryl group, a heteroaryl group, an alkyl group of 1 to 20 carbons, an alkenyl group, an alkynyl group, $-C(O)R^3$, $M((Rs')(Rf'))_3$, $OM((Rs')(Rf'))_3$ or $OOM((Rs')Rf'))_3$, wherein M is Si, Ge, or Sn, and wherein R^1 and R^2 are each independently the same or different H, an alkyl group, $-SO_2R^3$ or $-C(O)R^3$, wherein R^3 is an alkyl group or an aryl group, and wherein Rs and Rs' are each independently the same or different a spacer group, and wherein Rf and Rf' are each independently the same or different a fluorous group; carrying out a reaction to produce an organic product; and after producing the organic product, separating any excess of the fluorous reaction component and any fluorous byproduct of the fluorous reaction component using a fluorous separation technique. Several compounds have the formula:

$$X^1Sn(R)_n[Rs(Rf)]_{3-n},\ X^1X^2Sn[Rs(Rf)]_2 \text{ or } O{=}Sn[Rs(Rf)]_2.$$

Figure 1. A Schematic Illustration of the Use of a Fluorous Reaction Component in an Organic Transformation

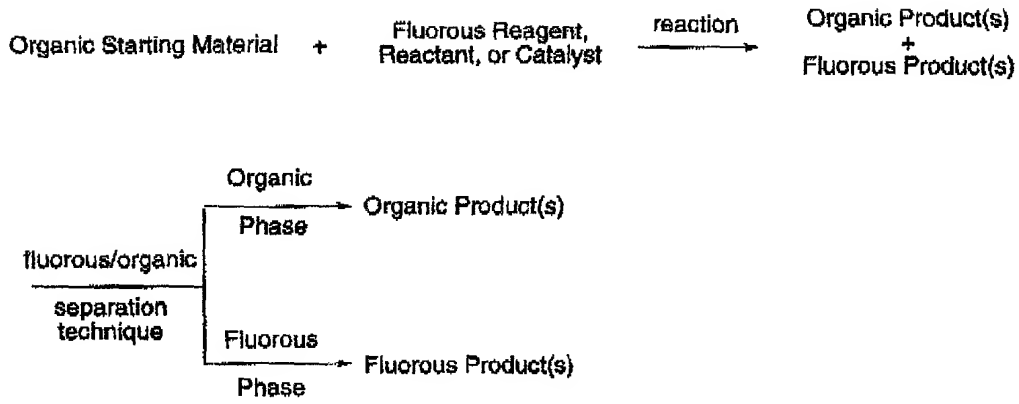
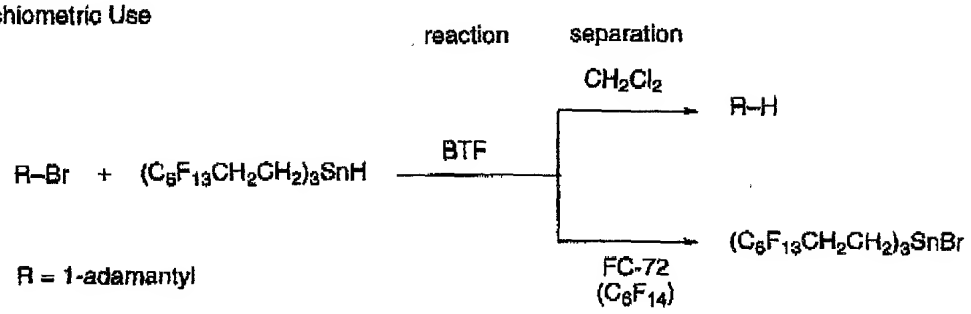


Figure 2. Illustrative Uses of Fluorous Tin Reagent $(C_6F_{13}CH_2CH_2)_3SnH$

Stiochiometric Use



Catalytic Use

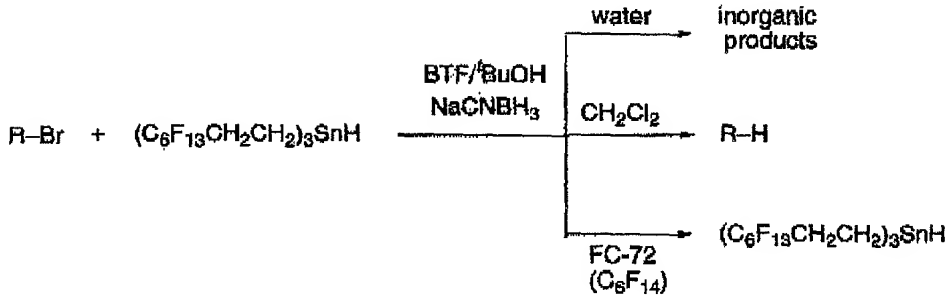
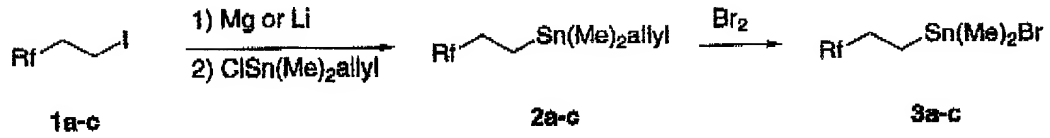


Figure 3. Representative Syntheses of Fluorous Tin Reagents Bearing One Fluorous Chain

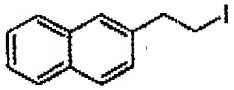


1a-c **2a-c** **3a-c**

a Rf = C_6F_{13}
b Rf = C_8F_{17}
c Rf = $C_{10}F_{21}$

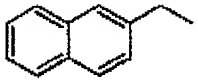
4a-c

Figure 4. Representative Reactions of Fluorous Tin Reagents Bearing One Fluorous Chain.



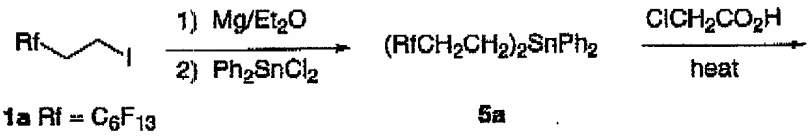
1) **4b** or **4c**
^{t}BuOH, $NaCNBH_3$

2) Fluorous-solid phase extraction

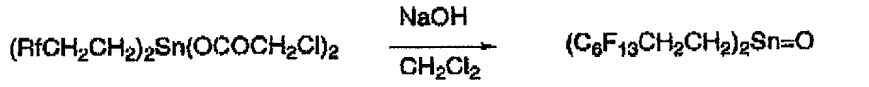


tin reagent	eluting solvent	yield
4b	85/15 MeOH/H_2O	83%
4c	100% CH_3N	83%

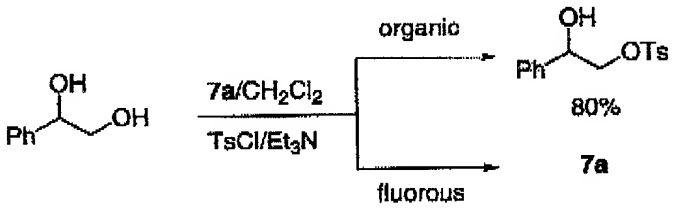
Figure 5. Synthesis and Use of Representative Fluorous Tin Reagents Bearing Two Fluorous Chains



1a Rf = C_6F_{13} **5a**



6a **7a**, exists as oligomer/polymer



either liquid-liquid or solid-liquid extraction can be used for the separation

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DECLARATION FOR UTILITY OR DESIGN PATENT APPLICATION (37 CFR 1.63)

☒ Declaration Submitted with Initial Filing OR ☐ Declaration Submitted after Initial Filing (surcharge (37 CFR 1.16 (e)) required)

Attorney Docket Number	00-012
First Named Inventor	DENNIS P. CURRAN
COMPLETE IF KNOWN	
Application Number	/ to be assigned
Filing Date	JUNE 22, 2000
Group Art Unit	to be assigned
Examiner Name	to be assigned

As a below named inventor, I hereby declare that:

My residence, post office address, and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint invento r (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

FLUOROUS TIN COMPOUNDS AND METHODS OF USING FLUOROUS TIN COMPOUNDS

(Title of the Invention)

the specification of which
☒ is attached hereto
OR
☐ was filed on (MM/DD/YYYY) _____ as United States Application Number or PCT International Application Number _____ and was amended on (MM/DD/YYYY) _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment specifically referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR 1.56.

I hereby claim foreign priority benefits under 35 U.S.C. 119(a)-(d) or 365(b) of any foreign application(s) for patent or inven tor's certificate, or 365(a) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's cer tificate, or of any PCT international application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application Number(s)	Country	Foreign Filing Date (MM/DD/YYYY)	Priority Not Claimed	Certified Copy Attached? YES	NO
			☐	☐	☐
			☐	☐	☐
			☐	☐	☐
			☐	☐	☐

☐ Additional foreign application numbers are listed on a supplemental priority data sheet PTO/SB/02B attached hereto:

I hereby claim the benefit under 35 U.S.C. 119(e) of any United States provisional application(s) listed below.

Application Number(s)	Filing Date (MM/DD/YYYY)

☐ Additional provisional application numbers are listed on a supplemental priority data sheet PTO/SB/02B attached hereto.

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DECLARATION — Utility or Design Patent Application

I hereby claim the benefit under 35 U.S.C. 120 of any United States application(s), or 365(c) of any PCT international application designating the United States of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application.

U.S. Parent Application or PCT Parent Number	Parent Filing Date (MM/DD/YYYY)	Parent Patent Number (if applicable)

☐ Additional U.S. or PCT international application numbers are listed on a supplemental priority data sheet PTO/SB/02B attached hereto.

As a named inventor, I hereby appoint the following registered practitioner(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith: ☐ Customer Number [ ] → *Place Customer Number Bar Code Label here*
OR
☒ Registered practitioner(s) name/registration number listed below

Name	Registration Number	Name	Registration Number
Henry E. Bartony, Jr.	34,772		

☐ Additional registered practitioner(s) named on supplemental Registered Practitioner Information sheet PTO/SB/02C attached hereto.

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. 1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Name of Sole or First Inventor: ☐ A petition has been filed for this unsigned inventor

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☐ Additional inventors are being named on the ____ supplemental Additional Inventor(s) sheet(s) PTO/SB/02A attached hereto

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DECLARATION

ADDITIONAL INVENTOR(S)
Supplemental Sheet
Page 1 of 1

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Name of Additional Joint Inventor, if any: ☐ A petition has been filed for this unsigned inventor

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Inventor's Signature						Date	
Residence: City		State		Country		Citizenship	
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